

Magnetic Anisotropy and Magnetization Dynamics of Individual Atoms and Clusters of Fe and Co on Pt(111)

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(Dated: March 19, 2009)

Abstract

The recently discovered giant magnetic anisotropy of single magnetic Co atoms raises the hope of magnetic storage in small clusters. We present a joint experimental and theoretical study of the magnetic anisotropy and the spin dynamics of Fe and Co atoms, dimers, and trimers on Pt(111). Giant anisotropies of individual atoms and clusters as well as lifetimes of the excited states were determined with inelastic scanning tunneling spectroscopy. The short lifetimes due to hybridization-induced electron-electron scattering oppose the magnetic stability provided by the magnetic anisotropies.

In modern magnetic recording, bits are stored in magnetically stable metallic grains, with larger densities being realized by reduced grain sizes. The magnetic stability is related to the grain's magnetic anisotropy energy (MAE) that has to be overcome to reverse the magnetization. Recently, a giant MAE of Co atoms on Pt(111) of 9.3 meV was found with X-ray magnetic circular dichroism (XMCD) [1]. This raised the hope for achieving the ultimate size limit in magnetically stable atoms or clusters at cryogenic temperatures. The challenge of studying magnetic stability lies in the direct investigation of a single atom, which is not possible by XMCD. We report here on the MAE and magnetization dynamics of single Fe and Co atoms and clusters on Pt(111) investigated with scanning tunneling microscopy (STM) and show that the quantum-mechanical nature of the magnetic system becomes essential.

To determine the MAE and the magnetization dynamics of individual atoms and small clusters, we performed inelastic tunneling spectroscopy (ITS) with a home-built low-temperature STM in ultra-high vacuum. The tunneling electrons may exchange spin angular momentum with these magnetic objects [2]. The result of such inelastic spin-flip scattering is a change of the magnetization direction of the object [3]. For Fe and Co atoms and clusters on Pt(111) the uniaxial anisotropy dominates and favors perpendicular anisotropy [1, 4]. In the quantum limit, i. e. for an isolated magnetic object with spin S , the uniaxial anisotropy energy can be written as DS_z^2 ($D < 0$ for easy axis out of plane). This description is linked to the classical uniaxial MAE $K \cos^2 \theta$ by the correspondence principle $\cos \theta = S_z/S$ (θ is the angle of the magnetization with respect to the surface normal). To relate the spin-flip energy E_{sf} of a tunneling electron to the MAE, we note that upon spin-flip scattering the magnetic cluster is excited from its ground state with $S_z = \pm S$ to a state with $S_z = \pm(S - 1)$, i. e. S_z of the object is changed by 1. For known S , K can be estimated as $E_{\text{sf}} \times S^2/(2S - 1)$ and $|D|(2S - 1) = E_{\text{sf}}$.

Inelastic spin-flip scattering shows up in ITS. This approach was so far restricted to atoms on insulating layers, e. g. Mn atoms on Al_2O_3 or CuN [2, 5] but failed in entirely metallic systems. Recently, we have shown that even in metallic structures (bulk samples and thin films) spin-flip scattering can be detected [3, 6, 7]. Here we extend this technique to single atoms and clusters on Pt(111). In metallic systems, elastic tunneling leads to a linear dependence of the tunnel current I on the bias voltage U in the low bias regime. If $eU = E_{\text{sf}}$, an additional inelastic tunnel channel opens and the slope of $I(U)$ is increased

for $eU > E_{\text{sf}}$. This change is usually too small to be identified directly. It can, however, be seen as a peak in d^2I/dU^2 [8, 9]. The excitation occurs for both tunneling directions, with a ‘negative peak’ appearing at negative bias.

To achieve a high surface quality, the Pt(111) substrate was cleaned by multiple cycles of Ar sputtering and annealing until contaminations were absent in STM images. W tips were cleaned in vacuum by flashing, such that the end of the tip melted. Small amounts (< 0.01 atomic layer) of Fe or Co were deposited on Pt(111) at 4.3 K, resulting in isolated adatoms. d^2I/dU^2 spectra were recorded for Fe atoms and the Pt surface (crosses in Fig. 1a). The second derivative was measured with a lock-in amplifier detecting the second harmonics in the tunnel current due to a 1.4 – 3.2 mV, 16.4 kHz modulated bias voltage. While spectrum (b) of the Fe atom on Pt(111) (see Fig. 1) clearly shows an ‘inelastic’ minimum/maximum structure, the Pt spectrum (c) displays a minute signal. The genuine excitation spectrum (d) is obtained by subtracting (c) from (b) and is found to be almost symmetric, with the minimum and the maximum reflecting inelastic excitations. An excitation energy of ≈ 6 meV is estimated from a Gaussian fit of peak and dip. Co atoms on Pt(111) give very similar results, providing ≈ 10 meV (see Fig. 1e).

The observed spectroscopic features are ascribed to spin-flip excitations since other possibilities can be excluded as follows. (i) Plasmons in Fe, Co and Pt have energies in the range of several eV. Besides, they cannot be confined to single atoms, and therefore do not explain the observed excitations. (ii) Atomic vibrations can be excluded by first-principles calculations. The vibration energies were obtained with the Vienna Ab initio Simulation Package (VASP) [10]. The potential landscape was mapped by moving the adatom from its equilibrium position in all directions. Within the harmonic approximation, the softest phonon was estimated to 27 meV for Fe and 24 meV for Co. These energies are significantly larger than the measured excitation energies. (iii) The Kondo effect could produce similar features in the spectra [11]. However, Fe and Co on Pt(111) show no Kondo effect: The perpendicular magnetic anisotropy of Co and Fe on Pt(111) [1, 4] lifts the spin degeneracy of the atom and hinders the exchange of electrons with opposite spins between the atom and the substrate [12, 13]. Further, being easily polarized, the magnetic moments at the Pt atoms adjacent to the adatom [1, 4, 14] counteract the Kondo screening. Thus, the observed inelastic features are clearly attributed to magnetic excitations.

To determine the classical MAE from the excitation energy, the spin S of the adsorbed

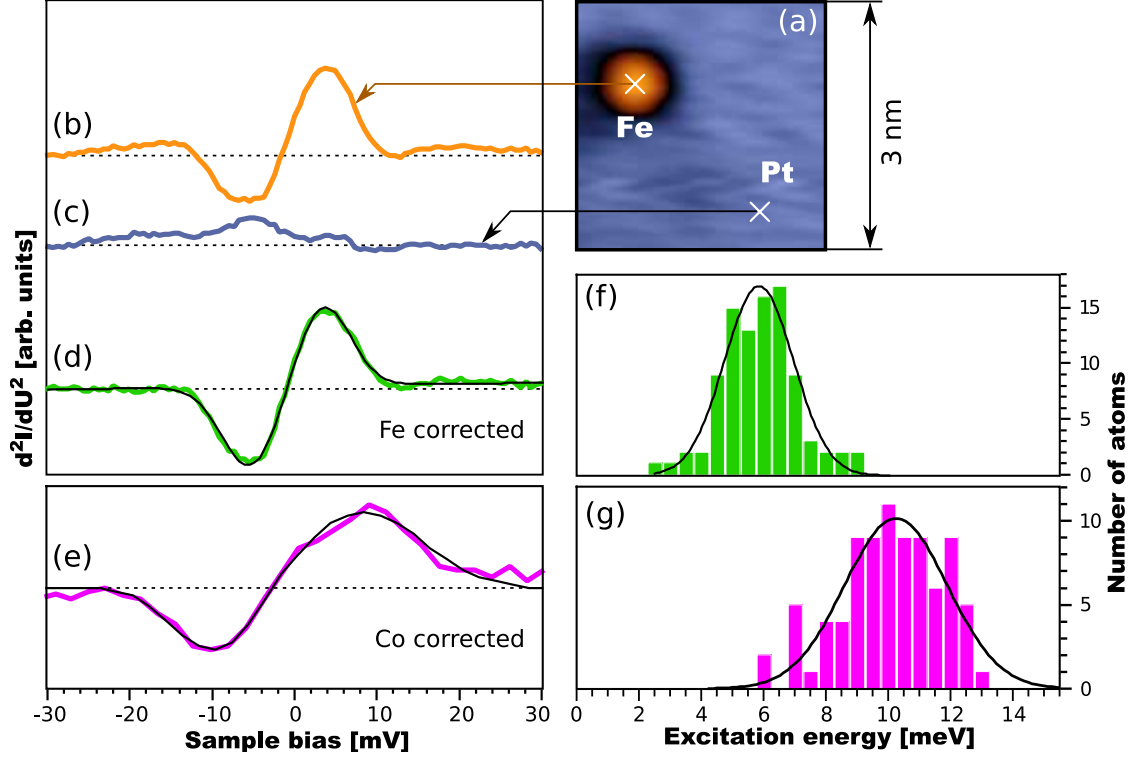


FIG. 1: (a) Topography of a single Fe atom on Pt(111). (b) d^2I/dU^2 spectra of an Fe atom on Pt(111), (c) of the bare Pt(111) background, and (d) the difference spectrum. (e) Background-corrected Co spectrum. Gaussian fits are shown in black. (f) Distributions of excitation energies for Fe atoms and (g) for Co atoms.

atom and the induced Pt moments must be known. We therefore calculated the latter from first principles within our scalar-relativistic Korringa-Kohn-Rostoker (KKR) approach. The large polarizability of Pt demands to treat an ‘extended impurity’ which comprises the adatom and 5 Pt layers with 16 Pt atoms each. The impurity is embedded in semi-infinite Pt(111) by solving the Dyson equation for the Green function. [15] Exact positions of the Fe and Co adatoms, which are crucial for calculating reliable electronic and magnetic properties, are obtained by VASP. [16, 17]. The adatoms are attracted by the surface but the inward relaxation does not strongly depend on the adsorption site (fcc or hcp). The adatom-tip interaction was simulated and found to reduce the inward relaxation by 2–3 %.

The total spin magnetic moments (adatom and adjacent Pt atoms) show a maximum at 25–30 % of inward relaxation and decrease with increasing atom–substrate distance (see Fig. 2). This originates mainly from the induced Pt magnetic moments while the local

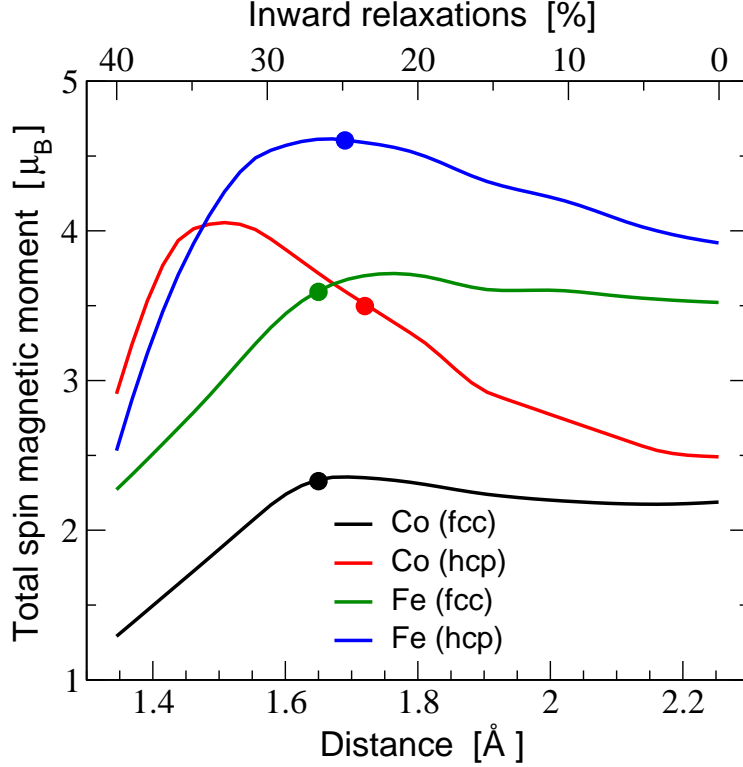


FIG. 2: Spin magnetic moments versus relaxation of the Fe and Co adatoms. The circles indicate the equilibrium distances.

magnetic moments of Co and Fe are not affected by relaxation. Assuming bulk positions for the adatoms results in significantly larger spin moments [1, 4].

From the total spin magnetic moment of $2.2 \mu_B$ for a Co adatom in an fcc position we deduce $S = 1$, assuming a Landé factor of $g \approx 2$. As a consequence, the excitation energy from the ground state with $S_z = 1$ to the excited state with $S_z = 0$ corresponds directly to the classical uniaxial MAE [18].

The excitation energies were measured repeatedly (see Fig. 1g). The distribution fitted with a Gaussian yields an average MAE of 10.25 meV per Co atom (cf. Table I). The result agrees well with the experimental observations on an ensemble of Co atoms using XMCD [1], thereby confirming our conclusion that the excitation is of magnetic origin. A similar analysis was performed for Fe adatoms. The total spin moment of $3.4 \mu_B$ for fcc sites results in $S = 3/2$. The Gaussian fit in Fig. 1f gives an average MAE of 6.53 meV per Fe atom (see Table I).

Single adatoms can occupy fcc or hcp threefold hollow sites on Pt(111). The potential

TABLE I: Measured excitation energies related to the MAE.

cluster	spin transition	excitation energy [meV]	MAE [meV/atom]
Co ₁	1→0	10.25±0.15	10.25±0.15
Co ₂	2→1	8.2±0.4	5.5±0.3
Co ₃	3→2	8.3±1.2	5.0±0.8
Fe ₁	3/2→1/2	5.83±0.08	6.53±0.09
Fe ₂	3→2	5.98±0.09	5.20±0.09
Fe ₃	9/2→7/2	6.5±0.2	5.5±0.2

barrier of ≈ 0.2 eV [19] for hopping from an fcc to an hcp site hinders thermal diffusion between the two positions at 4.3 K, suggesting that adatoms occupy both sites equally likely. Interestingly, the histograms for Fe and Co atoms are fitted well with a single Gaussian. This observation implies that either the excitation energies do not vary with position (within the resolution of ≈ 3 meV) or that only one of the two positions is occupied.

To corroborate the experiment we computed MAE's using our relativistic layer-KKR code, invoking the magnetic force theorem [20]. The MAE of a relaxed Fe atom is approximately 3.2 meV in fcc and 0.4 meV in hcp positions; for a Co atom we find 3.1 meV for fcc and 3.8 meV for hcp positions. These values are smaller than the experimental ones but of the same order of magnitude. The MAE for Fe in hcp position is significantly smaller than the experimental value, suggesting that Fe in the fcc position is mainly probed: Due to large tunnel currents, the adatoms are possibly moved to the more stable fcc sites. In case of Co, there is no significant difference in MAE on the hcp and fcc sites. The agreement with experiment is substantially better for Fe than for Co, pointing to the importance of correlation effects in systems with localized $3d$ electrons. In the present calculations, correlations are treated within the local spin density approximation (LSDA) which works better for Fe than for Co: The additional d electron (with respect to Fe) causes stronger correlations and requires to go beyond LSDA.

The probability of spin-flip scattering, as determined from the area under the inelastic peaks, is $\approx 2\%$ for both Fe and Co if the bias energy exceeds the MAE. This implies that at high bias even with tunnel currents in the pA range, the magnetic state of the atoms is

flipped at a rate too high to be observed in STM. This explains the absence of a hysteresis for single adatoms recently found at a sample bias of ≈ 200 mV [21]. Note also that the peaks in the spectra are rather broad, an effect accounted for by short lifetimes but not by thermal smearing or the lock-in modulation. Having corrected for experimental broadening [9], the widths of the inelastic peaks of Fe and Co are 5.6 meV and 18 meV, respectively, which correspond to lifetimes of the excited states of less than 60 fs for Fe and 24 fs for Co atoms. These lifetimes are shorter than the time between consecutive spin-flip events (≈ 0.5 ns at $I \approx 10$ nA with 2 % scattering probability). Therefore only excitations from the ground state are observed.

Lifetimes provide information on the magnetization dynamics which is not accessible by XMCD. The above lifetimes indicate efficient relaxation processes which are absent for magnetic ions in insulators [5]. Since comparable MAE's were found in metals and insulators, spin-orbit interaction can be ruled out as relaxation mechanism. More likely, the strong hybridization of the adatom states with those of the Pt substrate leads to efficient electron-electron scattering processes that relax the magnetic state of the adatom: The smaller hybridization of the Fe-3*d* states with the Pt-5*d* states as compared to Co leads to both a lower MAE and to a longer lifetime of the excited Fe state than that of Co.

Using the atomic manipulation capabilities of the STM [22], it is possible to extend the investigation to well-defined Fe and Co clusters composed of two and more atoms (here: dimers and trimers; Fig. 3a). The dimers—and even more trimers—appear significantly higher than single atoms in topographic scans (Fig. 3b; cf. Ref. 23).

To investigate the inelastic excitations of clusters we use the same approach as for single atoms. In Fe and Co clusters the local magnetic moments couple ferromagnetically, and the total spin of the cluster is obtained by adding individual spins. There are, however, two different types of spin-flip excitations in clusters, as illustrated by a low- and a high-energy excitations in the dimer spectrum in Fig. 3c. (i) At low energies, the magnetic moment of the entire cluster can be rotated collinearly, i.e. the total spin S of the cluster is rotated but its length stays constant. In analogy to single atoms we obtain the MAE of the cluster from this excitation energy (see Table I). In agreement with XMCD data and calculations [1], the MAE per atom drops with the size of the cluster. This is due to quenching of the orbital moment. While a single adatom on Pt(111) has a high rotational symmetry with respect to rotation about the surface normal, this symmetry is broken with adding another

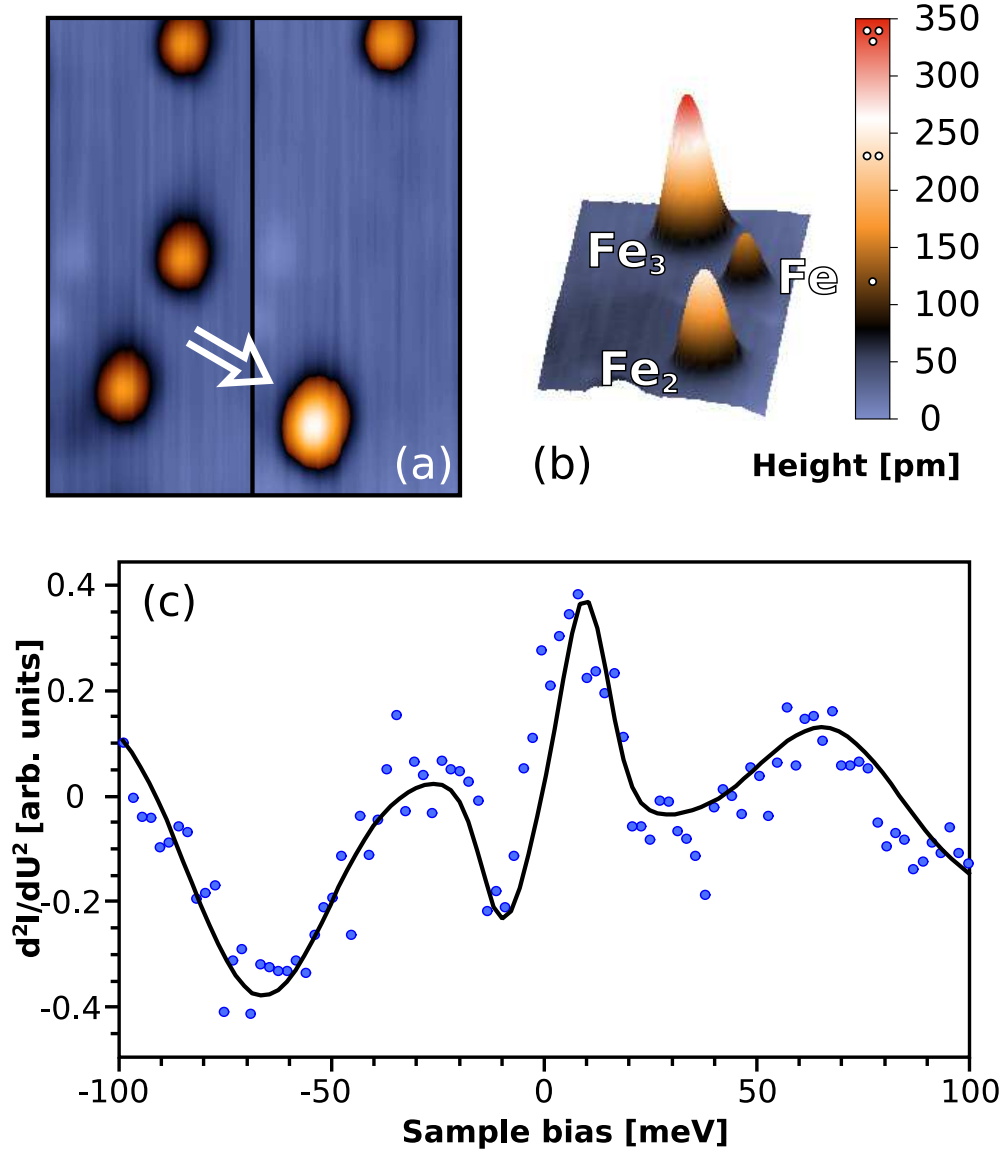


FIG. 3: (a) Formation of a Co dimer by manipulating two Co atoms by the STM [arrow]. (b) 3D view of an Fe atom, dimer and trimer. (c) d^2I/dU^2 spectra of an Fe dimer on Pt(111) with two excitations visible. Gaussian fits are shown as solid line.

atom. The third atom lowers the MAE only slightly. The experiment shows that such a tendency does not depend on the adatom species. The MAE's of Co trimers agree as well with XMCD data.

(ii) At higher energies, the 'inner' magnetic structure of the cluster can be excited into a noncollinear state. In addition to the anisotropy energy, exchange energy has to be paid, being typically one order of magnitude larger. High energy excitations appear in experiment

as broad peaks around 50 meV for Fe dimers (Fig. 3c). The width of 33 meV is caused by the short lifetime of the excited state (≈ 10 fs). An evaluation of 18 dimers gives an excitation energy of 54 ± 2 meV. Assuming a spin of $S = 3$ for the Fe dimer, the quantum-mechanical excitation energy is $3J - 5|D|$. With $|D| = 1.15 \pm 0.02$ meV, obtained from the first excitation, this gives an exchange constant J of 16 ± 1 meV. The extremely short lifetimes of the noncollinear state is due to the exchange interaction. This interaction conserves S_z but may alter S , so that a noncollinear state can rapidly decay into a collinear excited state with identical S_z . To elucidate this experimental finding we estimated the exchange energy of a Fe dimer on Pt(111) from first-principles calculations. The least-energy configuration is a dimer with Fe atoms occupying next-nearest neighbor fcc and hcp positions. The magnetic moments of $2.85 \mu_B$ per atom align parallelly and the exchange constant J is estimated to 11 meV, in agreement with experiment.

The classical MAE found for individual Fe and Co adatoms and clusters predicts stable magnetic configurations on the time scale of years at temperatures below 2 K. When treating the cluster as a quantum-mechanical system, tunneling between magnetic states has to be considered [24]. The magnetization tunneling is induced either by a transversal magnetic field (absent in our studies) or by an in-plane anisotropy. The threefold-rotational symmetry of the substrate results in MAE terms of at least sixth order which contribute only for $S \geq 3$ [25] and can thus be excluded for Fe and Co. An additional mechanism for spin reversal is, however, provided by the electron-electron interaction. Hybridization of the adatom states with those of the Pt substrate leads to short lifetimes and increased energy smearing of the excited state. Thus, an overlap of the ground state and the excited state is likely despite the large MAE's. It results in a nonzero transition probability between the degenerate ground states via an intermediate excited state.

In conclusion, the magnetic stability of atoms and small clusters is related to the hybridization in two opposing ways. On one hand, the hybridization increases the anisotropy, stabilizing the spin. On the other it decreases the lifetime of the excited state, hence destabilizing the spin. Only by decoupling these effects, the aim of magnetically stable atoms and clusters may be reached. The presented ITS approach will help to find the best combination of magnetic atoms and substrates to achieve this goal.

The authors acknowledge funding by the Japan Society for the Promotion of Science (T.M.) and the Deutsche Forschungsgemeinschaft (W.W.).

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$|S| < 3$. \hat{S}_+ and \hat{S}_- are the spin ‘ladder’ operators.